

## DESCRIPTION

METHOD OF PRODUCING CERAMIC MULTI-LAYER SUBSTRATE

## 5 Technical Field

The present invention relates to a method of producing a ceramic multi-layer substrate on which semiconductor devices, chip capacitors, and so forth are to be mounted.

## 10 Background Art

In production of ceramic multi-layer substrates on which semiconductor devices, chip capacitors, and so forth are to be mounted, ceramic green sheets useful for a substrate are laminated to each other to form an unfired ceramic laminate, and then, the laminate is fired. However, 15 in the case in which the unfired laminate is fired as it is, the unfired ceramic laminate is shrunk at firing, so that a dimensional error is caused.

Thus, for example, as described in Japanese Unexamined Patent Application Publication No. 4-243978, ceramic green 20 sheets useful for shrink-prevention, which are not sintered at the firing temperature of the unfired ceramic laminate, are arranged on both of the main surfaces of the unfired ceramic laminate, and the unfired ceramic laminate is fired 25 at a temperature which is higher than the sintering

temperature of the unfired ceramic laminate and is lower than the sintering temperature of the ceramic green sheets useful for shrink-prevention, and thereafter, the shrink-prevention green sheets are removed.

5       The specific method of removing shrink-prevention ceramic green sheets described in WO99/56510 is known, in which as a first method, spraying ceramic powder together with compressed air, as a second method, spraying water together with compressed air, and as a third method,  
10       spraying a mixture of ceramic powder with water together with compressed air are exemplified.

However, when the first, second, and third methods are individually used, the following problems occur.

That is, according to the first method, the removing  
15       capacity is low, since the spraying spot of the ceramic powder is small. Also, the positional accuracy in the processing range is not high. Thus, possibly, the processing becomes unstable. As a result, it is difficult to uniformly remove the ceramic green sheets used for  
20       shrink-prevention. Moreover, a large-scale apparatus is required to collect the sprayed ceramic powder and the powder of the removed ceramic green sheets. Thus, large-scale facilities are necessary, and the cost is high.

Then, according to the second method, a larger part of  
25       the shrink-prevention ceramic green sheets used can be

removed. However, in the following case, the shrink-  
prevention ceramic green sheets can not be removed. That is,  
if glass is contained in the unfired ceramic laminate, the  
glass component of the unfired ceramic laminate and the  
5 ceramic component of the shrink-prevention ceramic green  
sheets will bond to each other to form a reaction layer.  
This reaction layer can not sufficiently be removed simply  
by spraying water together with compressed air.

According to the third method, the green sheets can be  
10 removed more uniformly compared with the method of spraying  
ceramic powder together with compressed air. The removal-  
capacity is high compared with the method of spraying water  
with compressed air. However, according to this method, for  
re-use of the spraying ceramic powder, the ceramic powder to  
15 be sprayed is required to have an average particle size  
equal to or nearly equal to that of the ceramic powder of  
the shrink-prevention ceramic green sheets. If the particle  
size of the spraying ceramic powder is larger than that of  
the ceramic powder of the shrink-prevention ceramic green  
20 sheets, it will be difficult to remove the powder of the  
shrink-prevention ceramic sheets by means of a filter, and  
hence, the average particle size of the spraying ceramic  
sheets changes with a lapse of use-time. As a result, the  
removing-conditions for the shrink-prevention ceramic sheets  
25 change, and thus, it is difficult to carry out the

processing uniformly. On the other hand, if the average particle size of the spraying ceramic sheets is smaller than that of the shrink-prevention ceramic sheets, the shrink-prevention ceramic sheets can be removed by means of a filter. However, in the case in which the average particle sizes of the used ceramic powders are not significantly different from each other, a part of the spraying ceramic powder will be also removed by means of the filter. Thus, the average particle size of the spraying ceramic powder changes with a lapse of use-time. As a result, the removing conditions for the shrink-prevention ceramic sheets change. Thus, it is difficult to carry out the processing uniformly.

In view of the foregoing, the present invention has been devised. It is an object of the present invention to provide a method of uniformly removing a shrink-prevention ceramic sheet in production of a ceramic multi-layer substrate using the shrink-prevention ceramic sheet.

#### Disclosure of Invention

According to the present invention, there is provided a method of producing a ceramic multi-layer substrate which includes a step of preparing a composite laminate comprising an unfired ceramic laminate formed by lamination of a plurality of substrate ceramic green sheets, and a shrink-prevention ceramic green sheet arranged on at least one of

the main surfaces of the unfired ceramic laminate and being substantially incapable of being sintered at the firing temperature of the unfired ceramic laminate, a step of firing the composite laminate at a temperature at which the unfired ceramic laminate can be fired and which is lower than the sintering temperature of the shrink-prevention ceramic green sheet, and a step of removing the shrink-prevention ceramic green sheet subjected to the firing step, from the fired composite laminate, and is characterized in that the step of removing the shrink-prevention ceramic green sheet contains a first removing step of spraying a liquid material (particularly, water) and compressed gas (particularly, compressed air) against the shrink-prevention ceramic green sheet on the main surface of the composite laminate subjected to the firing step, and a second removing step of spraying ceramic powder, a liquid material (particularly, water), and compressed gas (particularly, compressed air) against the main surface of the ceramic multilayer substrate subjected to the first removing step.

Preferably, the method of producing a ceramic multilayer substrate according to the present invention further contains a step of supersonic-cleaning the ceramic multilayer substrate as a third removing step subsequent succeeding the first and second steps. Also, preferably, the method of producing a ceramic multi-layer substrate

according to the present invention further contains a step of spraying a liquid material (particularly, water) and compressed gas (particularly, air) against the main surface of the ceramic multi-layer substrate as a third removing  
5 step succeeding the first and second removing steps.

According to the method of producing a ceramic multi-layer substrate of the present invention, mainly a part of the shrink-prevention ceramic green sheet, which does not react with a glass component of the ceramic multi-layer  
10 substrate, can be removed in the first removing step of spraying a liquid material and compressed gas. Thereafter, a residual material which does not removed in the first removing step can be removed in the second removing step. Moreover, in the third removing step of supersonic-cleaning  
15 or spraying a liquid material and compressed gas, a residual material not removed in the second removing step, and also the ceramic powder sprayed in the second removing step can be removed. Thereby, the shrink-prevention ceramic green sheet can be uniformly removed.

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#### Brief Description of the Drawings

Fig. 1 is a schematic cross-sectional view of a ceramic multi-layer substrate according to the present invention.

Fig. 2 schematically shows a process of the method of  
25 producing a ceramic multi-layer substrate according to the

present invention.

Fig. 3 schematically shows a process of the method of producing a ceramic multi-layer substrate according to the present invention.

5 Fig. 4 is a schematic cross-sectional view of an interdigital electrode on the ceramic multi-layer substrate according to the present invention.

Fig. 5 is a schematic view showing the migration of an electrode on the ceramic multi-layer substrate.

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#### Best Mode for Carrying out the Invention

Hereinafter, the present invention will be described with reference to an embodiment.

#### First Embodiment

15 1. Process of Preparing Composite Laminate and Firing the Same

As shown in Fig. 1, a composite laminate 1 is prepared by laminating a plurality of ceramic green sheets 2 for a substrate conductive layers 3 to form an unfired ceramic  
20 laminate 4, and laminating and press-bonding shrink-prevention ceramic sheets 5 to both of the main sides of the unfired ceramic laminate 4. In the composite laminate 1, via-conductors 6 are formed to connect the conductive layers 3 provided at different heights. It is to be noted than the  
25 shrink-prevention ceramic sheets 5 may be provided on one of

the main sides thereof.

The substrate ceramic green sheets 2 may be prepared, e.g., by adding a binder, a plasticizer, and a solvent to ceramic powder, mixing them by means of a ball mill, an  
5 atractor, or the like to form slurry, and forming the slurry into a sheet with a thickness of about 25 to 200  $\mu\text{m}$  by a doctor blade method or the like.

As ceramic powder to form s substrate ceramic green sheet, so-called LTCC (Low Temperature CO-Fired Ceramic)  
10 powder may be used. For example, crystallized glass with a crystallized temperature of 600 to 1000°C may be used, or the crystallized glass having a ceramic filler such as alumina, zirconia, mullite, cordierite, anosite, silica, or the like added thereto may be used. Moreover, as a binder,  
15 for example, polyvinylbutyral, a methacrylic polymer, an acrylic polymer, or the like may be used. As a plasticizer, derivatives of phthalic acid or the like may be used. As a plasticizer, alcohols, ketones, chlorine type organic solvents, or the like may be used.

20 The conductive layer 3 includes a so-called surface conductor layer and an internal conductor layer. The conductor layer 3 is formed by printing conductor paste containing metal powder of Ag, Cu, or the like onto the substrate ceramic green sheet 2. Moreover, the via-  
25 conductor 6 provided for the composite laminate 1 is formed



by filling the conductor paste into a via-hole formed in the substrate ceramic green sheets 2.

The shrink-prevention ceramic green sheet 5 is prepared by the same production method as that for the substrate ceramic green sheet 2. However, the sintering temperature is higher than the temperature at which the substrate ceramic green sheets 2. For example, in the case in which ceramic powder having a sintering temperature of up to 1100°C is used for the substrate ceramic green sheets 2, alumina, zirconium oxide, aluminum nitride, boron nitride, mullite, magnesium oxide, silicon carbide, or the like may be used. Suitably, the average particle sizes of these ceramic powders are in the range of 0.5 to 4  $\mu\text{m}$ . If the particle size is too large, the shrink-controlling force for the substrate ceramic sheets becomes weak in some cases. Moreover, the surface of the formed ceramic multi-layer substrate becomes rough in some cases.

In press-bonding the substrate ceramic green sheets 5 to both of the main surfaces of the unfired ceramic laminate 4, the pressure applied for the press-bonding is suitably in the range of 10 to 200 MPa, and the temperature is suitably in the range of 40 to 90°C.

Thereafter, the composite laminate 1 is fired. Thus, the ceramic multi-layer substrate having the shrink-prevention ceramic green sheets 5 formed on both of the main

surfaces is prepared. In this case, the sintering temperature is required to be a temperature at which the unfired ceramic laminate 4, that is, the substrate ceramic green sheets are sintered and which is lower than the sintering temperature of the shrink-prevention ceramic green sheets 5. That is, the shrink-prevention ceramic green sheets are not sintered at the firing. That is, since the shrink-prevention ceramic green sheets are not shrunk during the firing, the shrink of the ceramic laminate in the plane direction is suppressed. Probably, this is because the glass component oozed out from the ceramic laminate at the firing and the shrink-prevention ceramic green sheets react with each other, and thus, the reaction layer is formed at the interface. Accordingly, the positional accuracy of conductor patterns provided on the ceramic laminate can be maintained high when it is subjected to the firing processing, and also, the disconnection thereof is suppressed.

## 2. First Removing Step

After the composite laminate is fired, a liquid material, together with compressed air, is sprayed against the shrink-prevention ceramic green sheets. At this time, the organic component such as a binder or the like has been fired out and removed from the shrink-prevention ceramic green sheets. Thus, the green sheets are in the porous

state. As a liquid material, an acidic aqueous solution, an alkali solution, an organic solvent, or the like may be used. Particularly, water is preferable from the viewpoints of the property with respect to the environments and the cost-

5 performance. Moreover, as compressed gas, nitrogen gas or the like may be used. Particularly, compressed air is desirable from the viewpoint of the cost performance.

As a method of spraying a liquid material together with compressed gas, e.g., a method using a plasto-nozzle as  
10 shown in Fig. 2 is exemplified. In particular, a ceramic multi-layer substrate 24, which has been subjected to a firing process, is placed on a stand 7. Thereafter, a sealed material (here, water) is sprayed against a shrink-prevention ceramic green sheet 25 formed on one of the main  
15 surfaces of the ceramic multi-layer substrate 24, while the sealed material 8 is accelerated with compressed gas 9. In this case, a mixture 11 of the water 8 and the compressed gas 9 is discharged through a nozzle 10, which is a discharge port of the plasto-nozzle. Then, the mixture 11  
20 is continuously sprayed while the nozzle 10 is sequentially scanned in direction A shown by the arrow in Figure.

In this case, the pressure of the compressed gas is desirably in the range of 147 to 539 kPa. If the processing is carried out at a pressure of less than 147 kPa, the  
25 removing capacity for the shrink-prevention ceramic green

sheet is inferior, since the spraying pressure is excessively low, and the production efficiency decreases. On the other hand, if the processing is carried out at a pressure of more than 539 kPa, the degradation of the nozzle  
5 10 is accelerated due to the pressure. Moreover, the consumption of the compressed gas 9 increases, which causes a high running cost and also may damage the ceramic multi-layer substrate 24. Here, the pressure of compresses gas means a pressure thereof in a piping before the spraying.

10 By carrying out the first removing step, a part of the shrink-prevention ceramic green sheet 25 which has not reacted with a glass component of the ceramic multi-layer substrate 24 is removed. As a result, the reaction layer formed by the reaction of the shrink-prevention ceramic  
15 green sheet 25 with the glass component of the ceramic multi-layer substrate 24 remains. Also, in some cases, the non-reacted part of the shrink-prevention ceramic green sheet 25, which does not react with the glass component of the ceramic multi-layer substrate 24, is not removed by the  
20 first removing step and remains. Fig. 2 exaggeratedly shows the state in which the shrink-prevention ceramic green sheet 25, while no residual material of the shrink-prevention ceramic green sheet 25 is shown in the drawing.

Powder recovered in the first removing step essentially  
25 consists of the ceramic powder generated from the shrink-

prevention ceramic green sheet. Therefore, the powder can be efficiently recovered and re-used as ceramic powder particularly for use in a shrink-prevention ceramic green sheet.

5 3. Second Removing Step

Thereafter, ceramic powder and a liquid material are sprayed, together with compressed gas, against both of the main surfaces of the ceramic multi-layer substrate which has been subjected to the first removing step. In this method, 10 for example, they are sprayed, using a plasto-nozzle in a manner similar to that described with respect to the first removing step. In Fig. 2, as a sealed material 8, a mixture of ceramic powder and water is injected. The ceramic powder, water, and compressed gas are discharged through the nozzle 15 10. Here, as a liquid material, an acidic aqueous solution, an alkali aqueous solution, an organic solvent, and so forth may be also used. From the viewpoints of the property with respect to the environments and the cost performance, particularly, water is desirable. As compressed gas, 20 nitrogen gas may be used. From the viewpoint of the cost performance, particularly, compressed air is desirable.

In this case, the pressure of the compressed gas is desirably in the range of 98 to 343 kPa. If the processing is carried out at a pressure of less than 98 kPa, the 25 removing capacity for the shrink-prevention ceramic green

sheets is inferior, since the spraying pressure is excessively low, and the production efficiency decreases. If the processing is carried out at a pressure of more than 343 kPa, cracks are ready to occur at the interfaces between the surface conductor layers and the ceramic multi-layer substrate. Thus, the bonding strength between the conductor layers and the composite laminate is reduced. Thus, inconveniently, peeling of the conductor layers in the plating step or the like occur in some cases. In this case, it is desirable that the pressure is smaller than that in the first removing step. That is, in the second removing step, the ceramic powder is used as abrasive grains. Thus, if the pressure of the compressed air is higher than that in the first removing step, the surface property of the ceramic multi-layer substrate, particularly, the surface properties of the conductor layers of the ceramic multi-layer substrate will be deteriorated in some cases.

Desirably, the average particle size of the ceramic powder for spraying is in the range of 9.5 to 40  $\mu\text{m}$ . If ceramic powder having an average particle size of less than 9.5  $\mu\text{m}$  is used, the removing capacity for the shrink-prevention ceramic green sheets is inferior, and the production efficiency is reduced in some cases. On the other hand, if ceramic powder having an average particle size of more than 40  $\mu\text{m}$  is used, the collision force is

large at spraying, so that cracks are ready to occur at the interfaces between the conductor layers and the composite laminate. Thus, the bonding strength is reduced, and inconveniently, the conductor layers are peeled and so forth in some cases in the plating step. Moreover, problems occur in that the processing of portions where the intervals between wirings are small is ready to be irregular and so forth, since the particle size is large.

When the second removing step is carried out, the most of a trace amount of residual materials on both of the surfaces of the ceramic multi-layer substrate, which have not been removed in the first removing step, are removed, due to the physical action of the liquid material (particularly, water), the ceramic powder, and the compressed gas (particularly, compressed air). The ceramic powder recovered in the second removing step essentially consists of the ceramic powder sprayed together with water. Therefore, the ceramic powder can be efficiently recovered and re-used particularly as ceramic powder to be sprayed.

#### 4. Third Removing Step

Thereafter, the ceramic multi-layer substrate which has been subjected to the first and second removing steps is cleaned by a supersonic wave method.

In this step, as shown in Fig. 3, a cleaning liquid is placed in a cleaning tank 12. The ceramic multi-layer

substrate 24 as a material to be cleaned is placed into a cleaning basket 14 disposed in the cleaning tank 12. Thus, supersonic waves are irradiated into the cleaning liquid 13 by use of a supersonic wave vibrator 16 connected to a  
5 supersonic wave vibrator 16. Examples of the cleaning liquid include a methylene chloride aqueous solution, a trichloroethylene aqueous solution, and so forth.

In the case, it is desirable that the ceramic multi-layer substrate 24 is set in the cleaning basket 14 so as to  
10 stand upright. In this step, residual materials which have not been removed in the first and second removing steps, and the ceramic powder sprayed in the second removing step and remaining on the surface are removed.

Desirably, the vibrator frequency employed in the  
15 supersonic cleaning is in the range of 40 to 100 kHz. If the processing is carried out at 40 KHz or less, the cavitation force is high, so that the substrate is caused to swing considerably during the processing. In the case of a substrate having a small thickness, the substrate is cracked  
20 in some cases. Conductor layers which position in the vicinity of the vibrating portion of the vibrator may be broken. Moreover, in the case in which the cavitation force is high, the removing capacity for the ceramic powder placed into the porous portions of the ceramic layer and the  
25 conductor layers is low. This will cause problems such as



irregular plating, abnormal deposition, and so forth. If the processing is carried out at 100 KHz or higher, the cavitation force is extremely low, and the removing effect on the ceramic powder (sprayed ceramic powder) remaining on the surface of the ceramic multi-layer substrate is reduced. This results in low production efficiency in some cases.

Desirably, the output per unit area of the supersonic vibrator is in the range of 0.2 to 2.0 W/cm<sup>2</sup>. If the processing is carried out at less than 0.2 W/cm<sup>2</sup>, the removing effect on the ceramic powder (sprayed ceramic powder) remaining on the surface of the ceramic multi-layer substrate on the like decreases, and the production efficiency is reduced in some cases. On the other hand, if the processing is carried out at 2.0 W/cm<sup>2</sup> or higher, the substrate is caused to swing considerably during the processing. In the case of a substrate having a small thickness, it is broken in some cases. Conductor layers which position in the vicinity of the vibrating portion of the vibrator are significantly damaged and broken in some cases. Moreover, the removing capacity for the ceramic powder placed into the porous portions of the ceramic layer and the conductor layers is low. This will cause problems such as irregular plating, abnormal deposition, and so forth.

When the supersonic cleaning is carried out, residual materials which have not been removed in the second removing

step, and the ceramic powder which has been sprayed in the second removing step, are removed from the main surfaces of the ceramic multi-layer substrate 24, due to the physical action of the cavitation and the chemical action of a cleaning agent.

#### Second Embodiment

Similarly to the above-described first embodiment, the composite laminate having the shrink-prevention ceramic green sheets formed on both of the main surfaces is prepared, and is subjected to the first and second removing steps.

#### 4' Third Removing Step

A liquid material is sprayed, together with compressed gas, against the ceramic multi-layer substrate which has been subjected to the first and second removing steps. In this case, e.g., the method using a plasto-nozzle as employed in the first removing step according to the first embodiment may be used. Here, as a liquid material, an acidic aqueous solution, an alkali aqueous solution, an organic solvent, and so forth may be also used. From the viewpoints of the property with respect to the environments and the cost performance, particularly, water is desirable. As compressed gas, nitrogen gas may be used. From the viewpoint of the cost performance, particularly, compressed air is desirable.

In this case, the pressure of the compressed gas is

desirably in the range of 147 to 539 kPa. If the processing is carried out at a pressure of less than 147 kPa, the removing capacity for the shrink-prevention ceramic green sheets is inferior, since the spraying pressure is  
5 excessively low, and the production efficiency decreases. On the other hand, if the processing is carried out at a pressure of more than 539 kPa, the degradation of the nozzle  
10 is accelerated due to the pressure. Moreover, the consumption of the compressed gas 9 increases, so that the running cost becomes high, and the ceramic multi-layer  
substrate 24 is damaged in some cases. In this case, it is desirable that the pressure is higher than that in the second removing step. Thus, if the pressure of the  
compressed air is lower than that in the second removing  
15 step, it will be difficult to remove the ceramic powder (sprayed ceramic powder) intruding into the surface of the ceramic multi-layer substrate in the second removing step.

#### EXAMPLE

20 Hereinafter, the present invention will be described with reference to specific examples.

#### EXAMPLE 1

First, 15 parts by weight of polyvinylbutyral, 40 parts by weight of isopropylalcohol, and 20 parts by weight of  
25 trol were added to 100 parts by weight of mixed powder

formed by mixing crystallized glass powder containing  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ , and  $\text{CaO}$  with alumina powder at an equi-percents by weight, and mixed with a ball mill for 24 hours to form slurry. The slurry was formed into a ceramic sheet with a thickness of 120  $\mu\text{m}$ . Thus, a ceramic green sheet for a substrate was formed.

Subsequently, Ag paste was screen-printed thereon in a predetermined position thereof. The ceramic green sheets for a substrate were coated as described above, and an interdigital electrode was formed. As shown in Fig. 4, an interdigital electrode 17 comprises first electrode fingers 18a formed on a first terminal 18, and second electrode fingers 19a on a second terminal 19 which are formed in opposition to each other on the substrate ceramic green sheet 2. The widths of the first electrode fingers 18a and the second electrode fingers 19a are 100  $\mu\text{m}$ , and the intervals between the first electrode fingers 18a and the second electrode fingers 19a are 100  $\mu\text{m}$ .

Then, 15 parts by weight of polyvinylbutyral, 40 parts by weight of isopropylalcohol, and 20 parts by weight of trol were added to 100 parts by weight of alumina powder, and mixed with a ball mill for 24 hours to form slurry. The slurry was formed into a ceramic sheet with a thickness of 120  $\mu\text{m}$  by a doctor blade method. Thus, a shrink-prevention ceramic green sheet was formed.

Then, six substrate ceramic green sheets were laminated, and also, the shrink-prevention ceramic green sheets were laminated to both of the main surfaces of the six substrate ceramic green sheets, respectively. Then, the sheets were  
5 press-bonded at a pressure of 150 MPa and a temperature of 60°C. Thus, a composite laminate was formed.

Thereafter, the composite laminate was placed on a tray made of an alumina plate with a flatness degree of up to 0.05% and a porosity of 70%, and heated at 600°C for 3 hours,  
10 and thereafter, pressed at a temperature of 900°C for 1 hour. Thus, the substrate ceramic green sheets were sintered.

Subsequently, in the first removing step, water together with compressed air having the respective pressures in the range of 147 to 539 kPa shown in Table 1, was sprayed  
15 for 120 seconds against the shrink-prevention ceramic green sheets provided on both of the main surfaces of the ceramic multi-layer substrate.

Thereafter, in the second removing step, water and alumina powders with the respective average particle sizes  
20 in the range of 9.5 to 40  $\mu\text{m}$  shown in Table 1, together with compressed air in the range of 98 to 343 kPa were sprayed for 120 seconds against residual materials on the ceramic multi-layer substrate after the first removing step.

Subsequently, in the third removing step, supersonic  
25 cleaning was carried out at a supersonic vibrator frequency

of 40 to 100 kHz and an output per unit supersonic vibrator of 0.2 to 2.0 W/cm<sup>2</sup> for 300 seconds.

As a result of the above-described steps, the ceramic multi-layer substrates of Samples 1 to 8 were formed.

5 Comparative Example 1

A composite laminate was formed and fired under the same preparation conditions as those in First Example. The shrink-prevention ceramic green sheets were removed from the composite laminate, not subjected to the second removing  
10 step. In particular, in the first removing step, water and compressed air with 539 kPa were sprayed for 120 seconds against the shrink-prevention ceramic green sheets provided on both of the main surfaces of the ceramic multi-layer substrate. Thereafter, in the third removing step,  
15 supersonic cleaning was carried out at a supersonic vibrator frequency of 40 kHz, an output per unit area of a supersonic vibrator of 0.2/cm<sup>2</sup> for 300 seconds. As a result of the above-described steps, the ceramic multi-layer substrate of First Comparative Example was produced.

20 Second Comparative Example 2

A composite laminate was formed and fired in the same conditions as those in Example First. Twenty samples were prepared. For these twenty samples not subjected to the first removing step, the second and third removing steps  
25 were carried out to remove the shrink-prevention ceramic

green sheets. In the second removing step, water and alumina powder with an average particle size of 9.5  $\mu\text{m}$ , together with compressed air with 98 kPa, were sprayed for 120 seconds against both of the main surfaces of the ceramic multi-layer substrate. Thereafter, in the third removing step, the twenty substrates were supersonic-cleaned at a supersonic vibrator frequency of 40 kHz and an output per unit area of a supersonic vibrator of 0.2/cm<sup>2</sup> for 300 seconds. For the twenty samples, the second and third removing steps were carried sequentially, out one by one from the first sample to the twentieth sample. After these steps, a ceramic multi-layer substrate of comparative example 2a (first sample) and a ceramic multi-layer substrate of comparative example 2b (second sample) were prepared.

Regarding the respective samples (samples Nos. 1 to 8, comparative example 1, and comparative examples 2a and 2b) prepared in EXAMPLE 1, COMPARATIVE EXAMPLE 1, and COMPARATIVE EXAMPLE 2, the appearances were examined, and the results were shown in Table 1, where a circular mark represents "no irregular-removal", and a cross mark does "irregular removal".

Thereafter, a palladium catalyst was given to the respective samples of the ceramic multi-layer substrates, and then, the cleaning was carried out, so that nuclei of the palladium catalyst were formed on the interdigital

electrode portion. Thereafter, electroless nickel plating was carried out. Thus, nickel plating was performed on the interdigital electrode portion. A voltage of 50 V was applied to the interdigital electrode portion under the conditions of 85°C and 85%RH for 1000 hours. Then, the insulation resistance was measured. Table 1 shows the measuring results.

Table 1

Sample Number	First removing step	Second removing step		Third removing step		Appearance of substrate	Insulation resistance LogIR (O)
	Pressure (kPa)	Average particle size (μm)	Pressure (kPa)	Frequency (KHz)	Output (W/cm <sup>2</sup> )		
No. 1	147	9.5	98	40	0.2	○	≥9
No. 2	539	9.5	98	40	0.2	○	≥9
No. 3	147	9.5	343	40	0.2	○	≥9
No. 4	147	40	98	40	0.2	○	≥9
No. 5	147	40	343	40	0.2	○	≥9
No. 6	147	9.5	98	40	2.0	○	≥9
No. 7	147	9.5	98	100	0.2	○	≥9
No. 8	147	9.5	98	100	1.0	○	≥9
Comparative example 1	539	Not processed		40	0.2	×	≤5
Comparative example 2a	Not processed (first sample)	9.5	98	40	0.2	○	≥9
Comparative example 2b	Not processed (twentieth sample)	9.5	98	40	0.2	×	≤5

10

## EXAMPLE 2

Similarly to EXAMPLE 1, the ceramic multi-layer



substrate having the shrink-prevention ceramic green sheets formed on both of the main surfaces was prepared. The first and second removing steps were carried out under the conditions shown in Table 2.

5        Thereafter, in the third removing step, water, together with compressed air in the range of 147 to 539 kPa, was sprayed for 120 seconds against the ceramic multi-layer substrate subjected to the first and second removing steps.

10        As a result of these steps, the ceramic multi-layer substrates of Samples Nos. 9 to 14 shown in Table 2 were prepared.

#### COMPARATIVE EXAMPLE 3

15        A composite laminate was formed and fired under the same preparation conditions as those described in EXAMPLE 2. The shrink-prevention ceramic green sheets were removed from the composite laminate, not subjected to the second removing step. In particular, in the first removing step, water and compressed air with 539 kPa were sprayed for 120 seconds against the shrink-prevention ceramic green sheets provided  
20        on both of the main surfaces of the ceramic multi-layer substrate. Thereafter, in the third removing step, water and compressed air in the range of 147 to 539 kPa were sprayed for 120 seconds. As a result of the above-described steps, the ceramic multi-layer substrate of Third  
25        Comparative Example was produced.

#### COMPARATIVE EXAMPLE 4

A composite laminate was formed and fired in the same conditions as those described in EXAMPLE 2. Thus, twenty samples were prepared. For these twenty samples not  
5 subjected to the first removing step, the second and third removing steps were carried out to remove the shrink-prevention ceramic green sheets. In the second removing step, water and alumina powder with an average particle size of 9.5  $\mu\text{m}$ , together with compressed air with 98 kPa, were  
10 sprayed for 120 seconds against both of the main surfaces of the shrink-prevention ceramic green sheets provided on both of the main surfaces of the ceramic multi-layer substrate. Thereafter, in the third removing step, water, together with compressed air in the range of 147 to 539 kPa, was sprayed  
15 for 120 seconds against the twenty samples. For the twenty samples, the second and third removing steps were carried out sequentially, one by one from the first sample to the twentieth sample. After these steps, a ceramic multi-layer substrate as comparative example 4a (first sample) and a  
20 ceramic multi-layer substrate as comparative example 4b (second sample) were prepared.

Regarding the respective samples (samples Nos. 9 to 14, comparative example 3, and comparative examples 4a and 4b) prepared in EXAMPLE 2, COMPARATIVE EXAMPLE 3, and  
25 COMPARATIVE EXAMPLE 4, the appearances were examined, and

the results were shown in Table 1, where a circular mark represents "no irregular-removal", and a cross mark does "irregular removal".

Thereafter, a palladium catalyst was given to the  
5 respective samples of the ceramic multi-layer substrates,  
and then, the cleaning was carried out, so that nuclei of  
the palladium catalyst were formed on the interdigital  
electrode portion. Thereafter, electroless nickel plating  
was carried out. Thus, nickel plating was performed on the  
10 interdigital electrode portion. A voltage of 50 V was  
applied to the interdigital electrode portion under the  
conditions of 85°C and 85%RH for 1000 hours. Then, the  
insulation resistance was measured. Table 2 shows the  
measuring results.

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Table 2

Sample Number	First removing step	Second removing step		Third removing step	Appearance of substrate	Insulation resistance LogIR (O)
	Pressure (kPa)	Average particle size (μm)	Pressure (kPa)	Pressure (kPa)		
No. 9	147	9.5	98	147	○	≥9
No. 10	539	9.5	98	147	○	≥9
No. 11	147	9.5	343	147	○	≥9
No. 12	147	40	98	147	○	≥9
No. 13	147	40	343	147	○	≥9
No. 14	147	9.5	98	539	○	≥9
Comparative example 3	539	Not processed		539	×	≤5

Comparative example 4a	Not processed (first sample)	9.5	98	539	O	$\geq 9$
Comparative example 4b	Not processed (twentieth sample)	9.5	98	539	x	$\leq 5$

As described above, in this example, the shrink-prevention ceramic green sheets could be uniformly removed, and moreover, the good insulation resistance could be maintained.

On the other hand, in the comparative example 1, the appearance showed the irregular removal, and the insulation resistance represented by LogIR was not more than 5.

In the comparative example 2, the appearance of the first ceramic multi-layer substrate showed no irregular removal, while that of the second ceramic multi-layer substrate showed irregular removal. Regarding the insulation resistance, the LogIR of the first ceramic multi-layer substrate was not less than 9, while that of the twentieth ceramic multi-layer substrate was not more than 5. That is, it has been revealed that the repetition of the second removing step causes the removing capacity for the shrink-prevention ceramic green sheets to be reduced.

In the comparative example 3, the appearance showed irregular removal, and the insulation resistance represented by LogIR was not more than 5.

In the comparative example 4, the appearance of the

first ceramic multi-layer substrate showed no irregular removal, while that of the twentieth ceramic multi-layer substrate showed irregular removal. Regarding the insulation resistance, the first ceramic multi-layer substrate had a LogIR of not less than 9, while the twentieth ceramic multi-layer substrate has a LogIR of not more than 5. That is, it has been revealed that the repetition of the second removing step causes the removing capacity for the shrink-prevention ceramic green sheets to be reduced.

The reason for the reduction in insulation resistance of the twentieth ceramic multi-layer substrates of the comparative examples 1 and 3 and the comparative examples 2 and 4 is as follows. That is, as shown in Fig. 5, a residual material 20 made from the shrink-prevention ceramic green sheets exists on surfaces of a ceramic multi-layer substrate 34. Thus, a part of the end faces 17a of the electrode 17 of the interdigital electrode is covered with the reaming material. The residual material 20 is porous. Thus, Migration of Ag occurs in the potion where no plating is performed, in the direction shown by an arrow, so that the insulation resistance is reduced.

#### Industrial Applicability

As described above, according to the method of

producing a ceramic multi-layer substrate of the present invention, ceramic multi-layer substrates having a high dimensional accuracy can be suitably produced at a high efficiency.